

New Raw Material for Thermoformable UV/EB Inks and Coatings

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Abstract

Printers and converters are constantly trying to develop new trends in packaging to attract consumers. One of these new trends, thermoformable packaging, is penetrating the narrow web market with great results. Formulating for energy-curable inks and coatings for these systems has been a challenge in the past with the limited number of raw materials that possess the necessary low viscosity and good formability. Sartomer has developed a new low viscosity oligomer, CN2285, that will expand the formulator's toolset for thermoformable systems.

Introduction

As each year passes UV/EB technology further penetrates into established graphics markets and creates new markets as well. A very good example of this is the implementation of UV flexo inks into the narrow and wide web processes. UV flexo technology has allowed printers to produce final products with much improved durability, while using a proven, environmentally green technology. The improvement in cured ink properties of UV flexo inks is now allowing printers to delve into new areas, such as retort and thermoformable packaging. UV/EB screen inks were the first energy-curable systems where the ink was printed, cured, then formed to a different shape. This process was used to decorate complex parts such as bicycle helmets and rigid packaging. These systems are high viscosity and depend on flexible urethane acrylate technology for their ability to thermoform.

For many thermoformable systems, such as UV flexo inks and UV/EB coatings, the use of flexible urethane acrylate oligomers poses a couple of issues. The first, and most obvious, is that flexible urethane acrylates have high molecular weights and thus have high viscosities. Using these oligomers requires the use of a lot of monomer to achieve the desired application viscosity. Monomer addition will lower the viscosity, but will also reduce the flexibility through increased cross-link density. The cross-link density removes the thermoplastic character of the ink or coating and disables the thermoformability of the overall system. Second, flexible urethane acrylates are flexible because they possess a low cross-link density and a T_g below room temperature. At room temperature, where the product will see most of its consumer contact, the product will not have the required scratch and scuff resistance. The ultimate goal of any thermoformable system would be to have excellent scratch and scuff resistance at room temperature but be dominated by thermoplastic behavior at the deformation temperature.

Experimental

Sartomer's new material for thermoformable UV/EB systems solves both the viscosity and final film property issues with unique chemistry. The goal at the start of the project was to design a low viscosity system that would not need additional monomer or oligomer to achieve the

desired thermoform properties. The desired viscosity of the new oligomer was set between 200 – 500 cps at 25° C. This would allow for its widespread use in UV flexo inks and coatings without the need for additional monomer. The viscosity constraints posed by urethane acrylates, irregardless of whether they are aromatic or aliphatic, instantly eliminated most of them from consideration. Even though this chemistry could not be considered, we were looking to achieve the same level of flexibility.

In many early generation UV/EB thermoformable systems isobornyl acrylate (IBOA) was used as the main diluent. This was for the two reasons already discussed. IBOA has a very low viscosity of only 8 cps at 25° C, making it the ideal diluent for urethane acrylates. IBOA, despite being monofunctional, has a homopolymer Tg of around 65° C. As a result, most systems formulated with IBOA will have a low cross-link density while possessing a Tg above 25° C. IBOA by itself is very brittle. But when it is combined with a flexible oligomer it will result in a very tough system. The biggest drawback to IBOA is the odor, and this has hampered its use in thermoformable packaging inks and coatings.

The intriguing combination of a Tg > 25° C and low viscosity make IBOA a very good model for any new thermoformable monomer or oligomer. With a Tg higher than room temperature, the thermoformable system would have very good scratch and scuff resistance, since it would still be in the glassy state. But the Tg also could not be too high. If it was, then the system may not have thermoplastic character at deformation temperatures. Typically films are formed at temperatures above 80° C with a ceiling of 120° C. So an oligomer was needed with a Tg above room temperature, but one that is well below 80° C.

Another component of successful thermoforming that was mentioned earlier was cross-link density. Systems that will thermoform readily are thermoplastic. Films such as PVC, PET, polyethylene, and polypropylene are thermoplastic and will readily deform upon heat and pressure. For UV/EB systems we will define thermoplastic as having low crosslink density. In this scenario a large percentage of the photopolymer chains within the cured system will not be connected through covalent bonds. However, chain entanglement and other bonding mechanisms, such as hydrogen bonding, may occur. This scenario is well represented in Diagram 1.

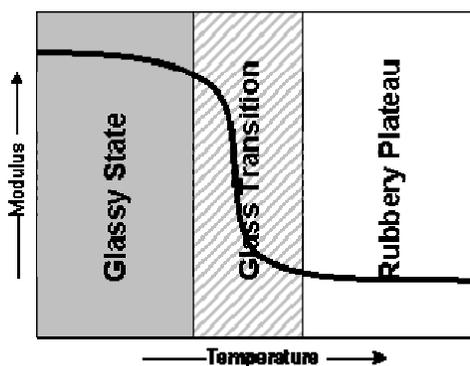


Diagram 1. Graphic representation of a thermoplastic system. The striped area represents the glass transition where the polymer changes from a glassy to a rubbery state.

Thermoplastic systems tend to have a more narrow glass transition between the glassy state and the rubbery plateau. When related to the physical properties of the system, this means that they will change properties fairly quickly. UV/EB systems, by their nature, are thermoset. Covalent cross-linking occurs during the photopolymerization that connects many different chains together. Thermoset systems possess a Tg, but it may have a very wide transition where the properties at various temperatures may be very similar. In the UV/EB industry the wide transition is used advantageously to give excellent scratch resistance, hardness, and other physical properties at varied temperature ranges. Diagram 2 represents this scenario.

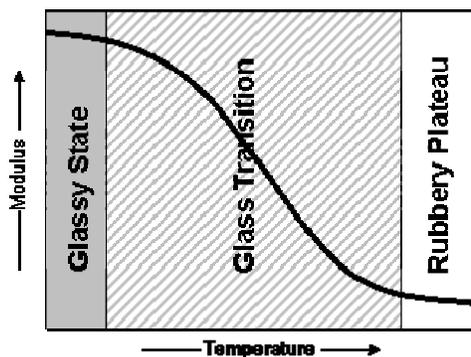


Diagram 2. Graphic representation of a thermoset system. The striped area represents the glass transition where the polymer changes from a glassy to a rubbery state.

For the development of the new technology the DMA graphs of various standard products were examined for their viscoelastic behavior. In the initial examination materials were looked at with various functionalities and various backbones. The materials can be found in Table 1.

	Structure	Functionality
Monomer 1	Aliphatic Monomer	Monofunctional
Monomer 2	Aliphatic Monomer	Monofunctional
Monomer 3	Aliphatic Monomer	Difunctional
Monomer 4	Aromatic Monomer	Difunctional
Oligomer 1	Aromatic Oligomer	Monofunctional
Oligomer 2	Aromatic Oligomer	Monofunctional

Table 1. Monomers and oligomers tested for project.

A close examination of the DMA graph (Diagram 3) for Monomer 1, which is IBOA, gives us the type of viscoelastic behavior that we desire from our new system. The analyses were run on a TA Instruments DMA2980 Dynamic Mechanical Analyzer. Each sample was run from -100° C to 250° C in multistrain mode at a 1.00 Hz frequency. A force of 0.5 N was applied to each sample before testing began. Samples were prepared on aluminum panels at a thickness of 0.4 mils and cured with two 300 W/in mercury arc lamps at 50 fpm for a total of 1500 mJ/cm² of UV irradiation.

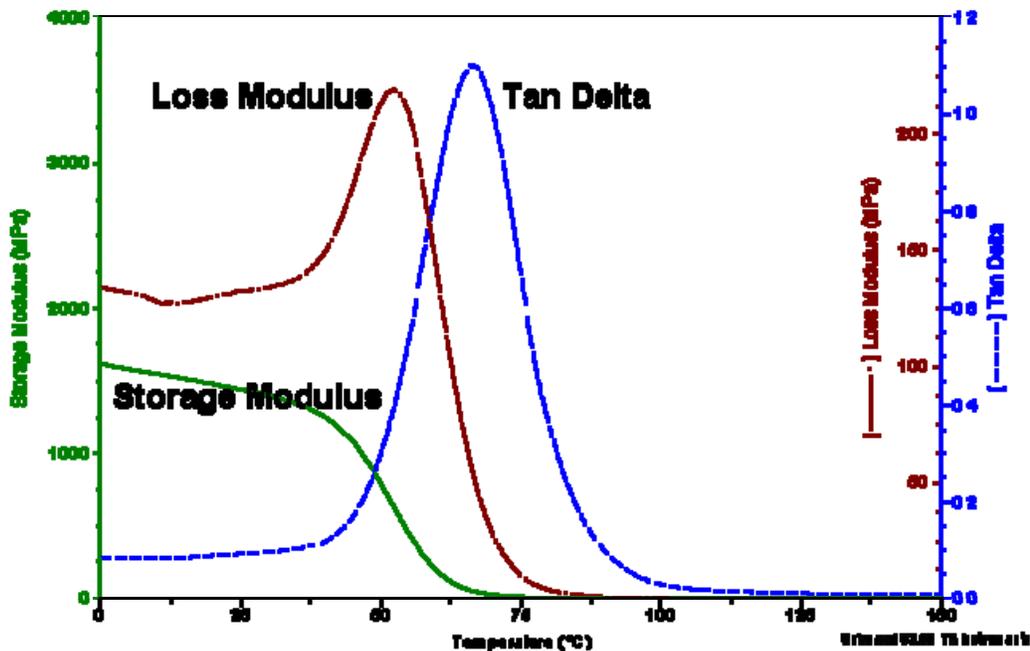


Diagram 3. DMA graph of Monomer 1 (IBOA).

In the DMA testing procedure the storage modulus, in Diagram 3 as the solid line, is an actual measurement of the viscoelastic properties of Monomer 1. The loss modulus, the line with the intermittent dots, is actually calculated by taking the first derivative of the storage modulus. This means that the peak of the loss modulus is actually the inflection point of the storage modulus. In all of our work the Tg and the mid-point of the glass transition is defined as this inflection point. The tan delta, the dashed line, is calculated as the ratio of the loss modulus to the storage modulus. So the peak of the tan delta coincides with the inflection point of the loss modulus. This is also the point when the storage modulus approaches zero and marks the beginning of the rubbery plateau.

For Monomer 1 (IBOA) the desirable attributes can be seen in Diagram 3. The Tg is 52° C, which is well above room temperature. This Tg gives the homopolymer of IBOA excellent hardness and scratch resistance. The start of the rubbery plateau is about at 66° C, far below the temperatures used in thermoforming. The IBOA homopolymer would be a rubbery solid, relatively speaking, when deformation occurred. Also, the storage modulus at 80° C and 100° C is only 9.8 and 8.1 MPa respectively. This low number indicates thermoplastic behavior resulting from low crosslinking of the IBOA homopolymer. The homopolymer undergoes a complete glass transition in only 52° C. As you can see, IBOA works well for thermoforming because it will be hard at room temperature, but will be pliable when exposed to the thermoform process.

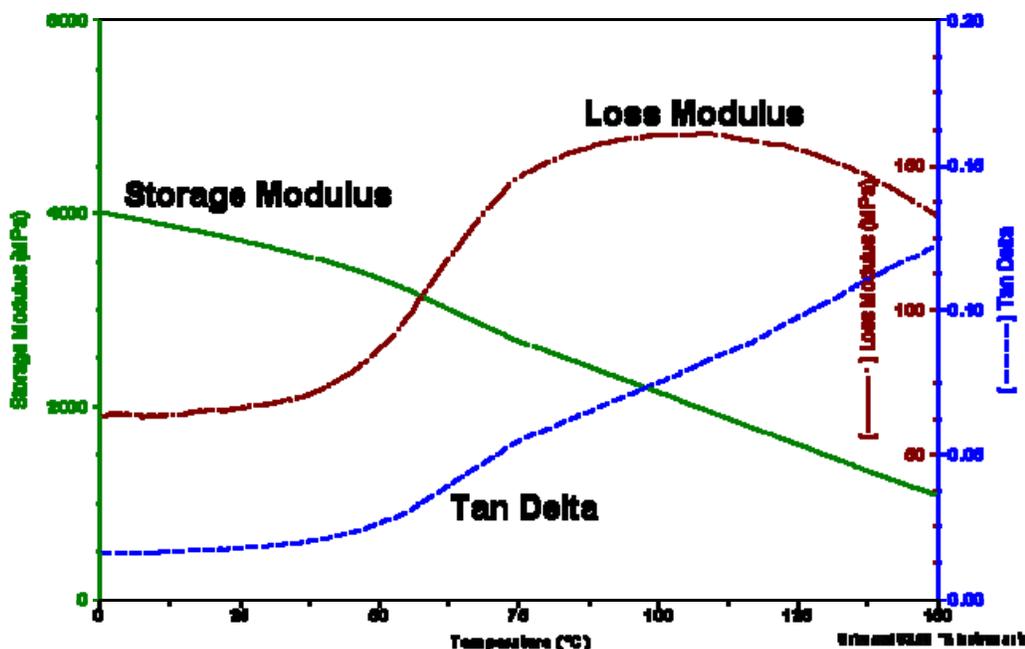


Diagram 4. DMA graph of Monomer 3.

Now compare this to a more cross-linked system based on Monomer 3. When using the same temperature scale in the graph you can see distinct differences between IBOA and Monomer 3. Monomer 3 is an aliphatic difunctional monomer with a T_g of 104°C . The homopolymer of Monomer 3 shows a very wide glass transition, which means that it has the same physical properties across a wide range of temperatures. The transition occurs over a 180°C range. Since the T_g is above room temperature, the homopolymer of Monomer 3 exhibits excellent scratch resistance and hardness. The rubbery plateau of this homopolymer does not start until 186°C , well above thermoforming temperatures. The storage modulus at that point is 414 MPa, which indicates much more cross-linking than what was seen in IBOA. The homopolymer of this product has thermoset behavior across a very wide range of temperatures. All of these reasons make Monomer 3 a very bad resin for thermoforming applications.

	Functionality	T_g ($^\circ\text{C}$)	Tan Delta ($^\circ\text{C}$)	Transition Width ($^\circ\text{C}$)	Storage Modulus at 80°C (MPa)	Storage Modulus at 100°C (MPa)
Monomer 1	Monofunctional	52	66	52	10	8
Monomer 2	Monofunctional	12	32	55	2	2
Monomer 3	Difunctional	104	186	180	2566	2147
Monomer 4	Difunctional	64	84	53	318	68
Oligomer 1	Monofunctional	12	26	47	1	1
Oligomer 2	Monofunctional	26	39	65	20	18

Table 2. Monomers and oligomers tested for project.

Many materials were tested for the applicability for this project. Based on viscosity and general viscoelastic behavior only six materials were examined more closely. Monomer 1 and Monomer 3 have already been examined. Monomer 2 looks like a good candidate since it is

monofunctional, has a narrow glass transition, and is thermoplastic at higher temperatures. The issue is that it is too low in T_g, so it is soft at room temperature. Monomer 4 is a difunctional monomer so it will not be as thermoplastic, but it has a T_g higher than room temperature and a narrow transition. Unfortunately there is too much cross-linking in the system and the system will not thermoform. Oligomer 1 is a low viscosity oligomer that possesses many of the same properties as Monomers 1 and 2 in that it is monofunctional with a narrow transition and a rubbery plateau that starts below thermoforming temperatures. Oligomer 1, like Monomer 2, has too low of a T_g to have good properties at room temperature.

Oligomer 2 was specifically designed for low viscosity thermoforming applications and meets all of the guidelines that have been set forth so far in this project. Now coded as CN2285, Oligomer 2 is a low viscosity oligomer that exhibits very good thermoformability up to 200% deformation. The properties of CN2285 are summarized in Table 3.

	CN2285
Viscosity – cps, 25° C	350
Specific Gravity – g/cm ³ , 25° C	1.16
Static Surface Tension – D/cm, 25° C	39.5
Refractive Index - 25° C	1.527
Color - APHA	150
Haze	Clear
Odor	Low

Table 3. Liquid properties of CN2285.

The viscosity of 350 cps allows CN2285 to be used in many low viscosity applications without the need for additional monomer that could cause thermoforming issues. CN2285 is a low color, low haze oligomer with a high refractive index. It is designed for all types of UV/EB applications including inks, coatings, adhesives, and electronics.

CN2285 fits all of the viscoelastic properties that were learned from the study of IBOA as a baseline material. The DMA graphs can be found in Diagrams 5 and 6. The T_g of CN2285 is 26° C, right at room temperature which gives the oligomer the good scratch and abrasion resistance but also a degree of flexibility. The oligomer has a rubbery plateau that starts at about 39° C, well below the typical thermoforming temperatures for various films. Also, the glass transition of CN2285 is only 65° C wide. This is not as narrow as the other materials tested, but still allows the oligomer to still perform well.

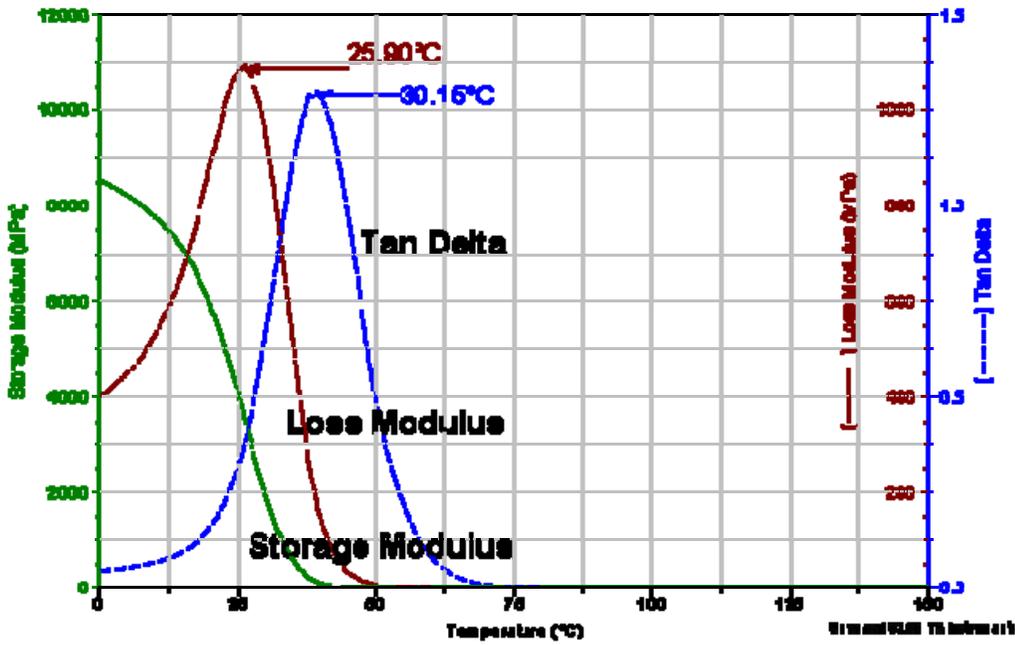


Diagram 5. DMA graph of CN2285 at the same temperature ranges as Diagrams 3 and 4.

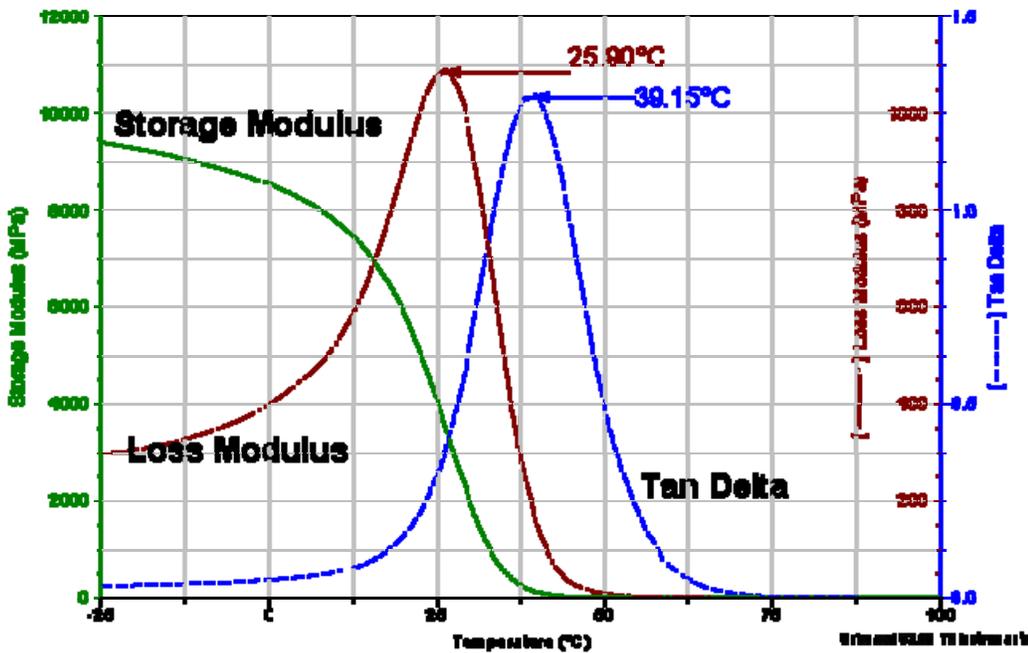


Diagram 6. DMA graph of CN2285 from -25° C to 100° C.

The viscoelastic properties of CN2285 can be directly related to the mechanical properties at room temperature. Samples were prepared on aluminum panels at a thickness of 0.4 mils and cured with two 300 W/in mercury arc lamps at 50 fpm for a total of 1500 mJ/cm² of UV irradiation. This is the same curing regime used for the DMA samples. An Instron Tensile Tester Model 5543 was used for the tensile, elongation, and 1% modulus testing. The results are listed in Table 4 for all mechanical properties for CN2285.

	CN2285
Tensile Strength - psi	2,200
1% Modulus - psi	10,500
Elongation - %	120
Tg by DMA - ° C	26
Tan Delta by DMA - ° C	39
Shrinkage - %	8

Table 4. Mechanical properties of CN2285 at room temperature.

As you can see, CN2285 still possesses good flexibility at room temperature. This is due to the Tg of the material being right at or just above room temperature. The oligomer has a unique combination of good elongation with a good modulus and tensile strength, making the CN2285 very tough. The oligomer also has low shrinkage due to its low functionality and bulky backbone.

So far the development of CN2285 and its properties have been discussed. But how do these properties actually relate to the applications for which this new oligomer was designed? Lets start with a discussion of how the thermoforming testing was performed. In our testing we used 1 mil PVC film, which is commonly used in thermoform systems. PET is another plastic that is commonly used for this application. In our application lab we used a dye heated to either 80° C or 100° C for the deformation. Diagram 5 represents the deformation using a dye with a semicircle end. If you work out the geometry, the deformation percent (%) is $57d^2$. So for a 1 inch diameter dye, which we used in our studies, the plastic film and the coating would be deformed 57%.

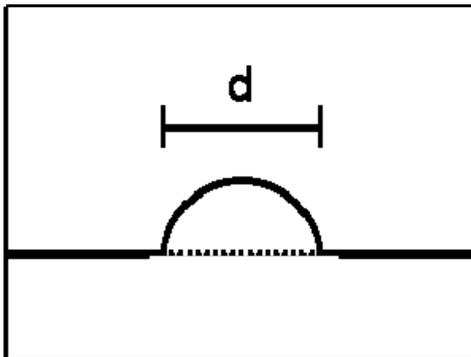


Diagram 5. Simple deformation using a dye with a semicircle end.

But deformation is rarely as simple as in Diagram 5. Diagram 6 represents a deeper draft thermoform system.

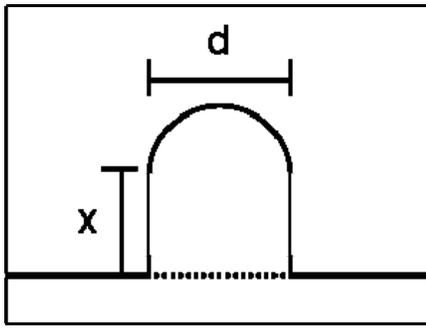


Diagram 6. Complex deformation with a draw and a semicircle end.

The total deformation, in distance, of this system would be $\pi d + 2x$. This would represent more complex packaging, such as cosmetic packaging.

Two systems based on CN2285 were examined for thermoformability. The first was a clear coating and the second was a pigmented flexo ink. The coating was simply the CN2285 with a PI, defoamer and wetting aid. This formulation can be found in Table 5.

Component	%	Purpose or Structure
CN2285	95.0	General coating properties and thermoformability
Lamberti Esacure® KIP100F	3.0	Oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone]
Lamberti Esacure® TZT	1.0	Blend of Methylbenzophenone and Trimethylbenzophenone
Byk®-088	0.5	Silicone defoamer
Byk®-UV3510	0.5	Silicone wetting aid

Table 5. Coating formulation based on CN2285.

Also a small amount of magenta dye was added to aid in seeing the failures during deformation. The coating was printed onto PVC film using a Cavanaugh handproofer with 600 line anilox roll. The coating was then cured at 150 fpm on a Fusion 600 W/in H lamp for an integrated energy of 82 mJ/cm² on an International Light IL390 radiometer. The coating showed excellent crosshatch adhesion to the PVC film when tested with 3M 610 tape. The coating (and film) were deformed at two different temperatures, 80° C and 100° C. To perform the deformation the stainless steel dye was heated to the desired temperature, then secured in the testing rig. The coated film was then deformed until visible cracks and separation were seen between either the coating itself or the coating and the film. The results of this testing can be seen in Table 6.

Deformation Temperature	% Deformation	Failure
80° C	180%	Coating to film
100° C	205%	Coating to film

Table 6. Deformation results for the coating formulation in Table 5.

The coating showed better ability to deform at 100° C, which corresponds to the viscoelastic behavior we examined earlier. At 100° C the CN2285 has a storage modulus of only 18 MPa, compared to 20 MPa at 80° C. In both cases the failure mode was a loss of adhesion between the coating and the film. After the deformation the scratch resistance was tested and found to be the same as before.

The second system evaluated for thermoformability was a UV flexo ink. The formulation can be seen in Table 7.

Component	%	Purpose or Structure
CN2285	56.0	General properties and thermoformability
Ciba® Irgalite® Blue GLVO	20.0	Cyan pigment
CN116	10.0	Epoxy acrylate for pigment dispersion
Solsperse® 39000	4.0	Hyperdispersant
Ciba® Irgacure® 369	3.5	2-Benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone
Lamberti Esacure® KS300	3.0	Alpha-hydroxycyclohexyl-phenyl ketone
Lamberti Esacure® TZT	1.0	Blend of Methylbenzophenone and Trimethylbenzophenone
Esacure® ITX	0.5	Isopropylthioxanthone
Shamrock UV636	1.0	Polyethylene wax dispersion in TPGDA
Byk®-088	0.5	Silicone defoamer
Byk®-UV3510	0.5	Silicone wetting aid

Table 7. UV flexo ink formulation based on CN2285.

This flexo ink was run 5 times over a three-roll mill at 40 rpm. To aid in pigment dispersion, CN116, a fatty acid modified epoxy acrylate, and Solsperse® 39000 were added. The ink showed good pigment dispersion with the addition of these two components and a final viscosity of 620 cps at 25° C. Again, the ink was printed onto PVC film using a Cavanaugh handproofer with 600 line anilox roll. The ink was then cured at 150 fpm on a Fusion 600 W/in H lamp for an integrated energy of 82 mJ/cm² on an International Light IL390 radiometer. The ink showed excellent crosshatch adhesion to the PVC film when tested with 3M 610 tape. The ink was then subjected to the same deformation as the coating. The results can be found in Table 8.

Deformation Temperature	% Deformation	Failure
80° C	145%	Coating to film
100° C	170%	Coating to film

Table 8. Deformation results for the coating formulation in Table 7.

The ink was actually not able to deform as far as the coating was. This is due to the addition of the CN116, the pigment, and the hyperdispersant. At both temperatures the failure was adhesion to the substrate.

Conclusion

The coating and ink application testing proves the applicability of CN2285 to clear and pigmented thermoformable systems. Our new oligomer allows for the development of unique and low viscosity systems that can be effectively deformed. CN2285 adds another tool to the ever-expanding toolbox that a formulator has at their fingertips for the development of new UV/EB technologies. The combination of unique chemistry, formulating strategy, and unique printing processes will continue to drive the development of new, eye-catching packaging.

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